Indian J. Phys. **69A** (1), 65 – 75 (1995)

I J P A
- an international journal

Magnetism and correlated electron systems

K. Ghoshray
Saha Institute of Nuclear Physics,
1/AF, Bidhannagar, Calcutta-64, India.

Abstract: This review is concerned with the experimental results of some magnetic materials which exhibit unusual behaviour of the magnetisation with temperature compared to those for normal ferromagnetic, antiferromagnetic and ferrimagnetic compounds. The results of magnetic susceptibility, NMR and Mössbauer studies are discussed with a brief introduction of the application of NMR and Mössbauer spectroscopy for understanding the magnetic properties of solids.

Keywords: Magnetism, Low-dimensional system, Spin glass, Heavy fermions.

PACS nos: 75.50.-y

1. Introduction.

In recent years various types of magnetic materials have been discovered, showing unusual behaviour with temperature compared to those of normal ferromagnetic, antiferromagnetic and ferrimagnetic systems. Further, many new phenomena are observed in solids for which correlation effects among the electrons appear to be important. Some of these discoveries were made on systems where the low-dimensional aspects are essential, whereas, for other classes such as heavy fermions, strongly correlated electrons in three dimensional solids are concerned. The present review is concerned with the experimental results mainly of susceptibility, NMR and, Mössbauer studies of three types of magnetic materials viz., 1. low dimensional systems, 2. spin glass systems, and 3. heavy

fermion systems. In section 2, a brief account will be given of how NMR and Mössbauer spectroscopy can provide information about the magnetic properties of solids. Sections 3, 4, and 5 will be devoted to the experimental results on above three types of systems.

2. NMR spectroscopy.

If we consider a solid containing atoms with non zero nuclear spin I, then it will have the magnetic dipole moment $\gamma\hbar$I, which will interact with the applied external magnetic field, H_o and the interaction Hamiltonian is $H = -\gamma\hbar I.\ H_0$ with energy eigen value $E=-\gamma\hbar H_0 m$. By application of a r.f. field of frequency, ν_o one can observe the transition between the Zeeman split levels. If in addition to the nuclear moments, there are atoms containing electronic moments, the nuclear moments can interact with these electronic moments through the hyperfine interaction $=-\gamma\hbar IH(t)$. The magnetic field, H(t) produced by the electrons at the nuclear site, is time dependent because of the fast flipping of the electronic spin due to various relaxation effects and exchange interactions. So, the total field at the nuclear site is $H=H_0+H(t)$. The time averaged part of H(t) produces a shift of the resonance line either towards low field or towards high field with respect to H_0 depending on the sign of $<H(t)>$. Further, $<H(t)>$ is proportional to the spontaneous magnetisation in the ordered state and the static susceptibility in the paramagnetic state. Fluctuating part of H(t) induces the spin- spin (T_2) and spin-lattice (T_1) relaxation times of the nucleus. The relaxation rates in this case are related to the Fourier transform of the electron spin pair correlation function $G(r_{ij},t)$ by the relation[1]

$$T_i^{-1} = \sum_{\alpha}\sum_{q} C_{\alpha}^{i} A_q^{\alpha} S(q,\omega), (i = 1,2) \qquad (1)$$

C_{α}^{i} depends on the nucleus and $S(q,\omega)$ is the Fourier transform of the electronic spin pair correlation function, $G(r_{ij},t)$. The q components of $S(q,\omega)$ are weighted by the A_q^{α} factor because the relaxation rates involve

both the auto and pair correlation function of the electron spins. Therefore the study of the relaxation rates of the nucleus can provide information about the electron spin dynamics during the transition. Close to the magnetic ordering temperature (T_c) where the fluctuaion of the critical wave vector (q_c) dominates, the temperature dependent line width δH ($\sim T_2^{-1}$), in NMR is related to $\delta H \propto \epsilon^{-\gamma+\nu(d-z)}$ where d denotes the lattice dimensionality, γ and ν are the static critical exponents and z is the dynamic exponent, ϵ is the reduced temperature, $(T-T_c)/T_c$. So from the temperature dependent line width or the spin lattice relaxation rate near T_c, one can determine z, knowing the static exponents γ and ν, from other experiments.

Mössbauer Spectroscopy

The phenomena of the emission of gamma rays from nuclei and their resonance absorption by identical nuclei without any loss of energy due to recoil is known as Mössbauer effect. The recoil energy produced in gamma ray emmision is in fact taken up by the entire lattice. In a microscopic description, a certain fraction of the γ ray photon emitted by the nuclie will emerge without exciting any phonons. The time averaged

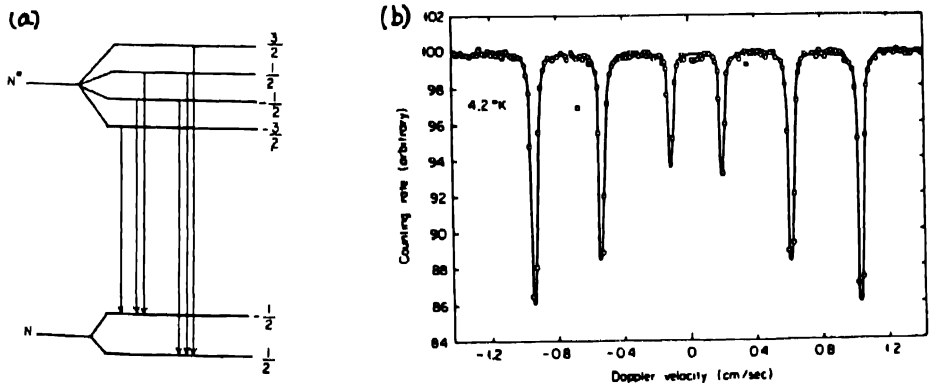

Fig.1 (a) Hyperfine structure in the nuclear excited state N* and ground state N of ^{57}Fe showing the six hyperfine transitions (neglecting the quadrupolar splitting) (b) Mössbauer spectrum of FeF_3 at 4.2K [1].

hyperfine field, <H(t)> produced at the nuclear site by the electronic moments produces a Zeeman splitting of the nuclear ground and excited states. In the magnetically ordered state, the magnitude of this splitting is considerably large (Fig.1) and the resonance pattern will arise from various transitions between the sublevels of the ground and excited state manifold. Figure 1 shows the hyperfine split spectrum of ^{57}Fe in a magnetically ordered solid. In the paramagnetic state normally no such splitting is observed due to hyperfine interaction because the larmor frequency of the nucleus (ν_L) in the time averaged hyperfine field <H(t)> is much smaller than the fluctuation frequency (ν_c) of H(t). As a result the magnitude of the hyperfine splitting becomes smaller than the intrinsic width of the Mössbauer resonance line, which is the life time of the nuclear excited state. However, if in the paramagnetic state, $\nu_L \sim \nu_c$ a considerable change is observed across T_c, either in the shape or in the width of the hyperfine components. In this case study of the resonance line width can provide information about the electron dynamics near T_c.

3. Magnetic properties of low dimensional systems.

The magnetic properties of a system of paramagnetic ions coupled in a linear chain (1d) or within a plane (2d) are of considerable interest both theoretically and experimentally[2] due to great simplifications which one obtains with respect to 3d systems. In these systems the topological restrictions alter significantly the spin dynamics i.e., even at higher temperatures where kT $\sim$ exchange interaction within the plane or a chain, short range order tends to develope and one can observe the fluctuations of local order over a relatively large temperature range. As a result of this the difference in the susceptibility maximum and T_N for antiferromagnetic ordering increases[3] as the dimensionality of the magnetic interaction decreases from 3d to 2d and 1d. Predominance of the short range order also extends the specific heat tail more above T_c for 2d and 1d systems compared to 3d [3]. Since NMR is a useful tool to probe

the effect of local field fluctuations, the low dimensional systems offer an opportunity to probe this effect near T_c through the measurement of line width δH ($\sim T_2^{-1}$), or T_1^{-1}. Fig. 2 shows the ^{19}F NMR line width in $AFeF_4$ (NH_4, Rb, K) type layered compounds [4] which are known to be two dimensional antiferromagnets from magnetic susceptibility data.[4] In these compounds, the fluorine atoms belonging to the FeF_6 octahedra experience two types of magnetic environment, since the axial fluorine F_I is linked with single Fe^{3+} ion and the planner fluorines are linked with two Fe^{3+} ions. Fig. 2(a) shows that for both types of fluorines, the resonance lines start to broaden from far above T_N. Fig. 2(b) shows δH, in case 3d system, MnF_2 [5] near T_N. Thus the line-width behaviour clearly reveal the predominence of short range order effect in 2d systems.

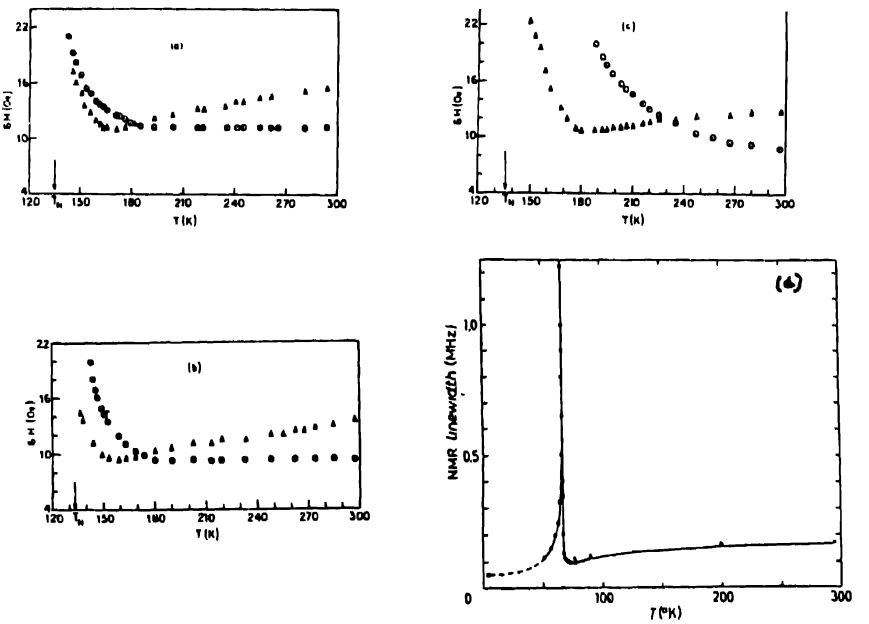

Fig.2 Variation of ^{19}FNMR line-width, δH of F_I (⊙) and F_{II} (▲) fluorines for (a) NH_4FeF_4 (b)$RbFeF_4$ (c) $KFeF_4$ at 15MHz [4], (d) ^{19}F NMR line-width in MnF_2[5].

The log-log plots of the line width versus ϵ show that for all the com-

pounds, the line widths are well described by straight lines over a certain temperature range obeying the law $\delta H \propto \epsilon^{-w}$. The values of w obtained from these plots when compared with those predicted by the current theory of critical dynamics[4] indicate that the exchange interactions in NH_4, and Rb, compounds are more close to 3d Heisenberg type whereas in K-compound , it resembles well with 2d Ising model. Interestingly, no such difference was emerged from bulk susceptibility measurements. Fig. 3 shows the behaviour of proton spin lattice relaxation rate, T_1^{-1} as a function of temperature, of

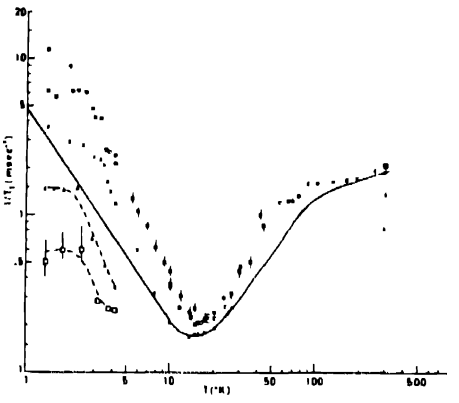

Fig.3 Proton spin-lattice relaxation rate in TMMC as a function of temperature and at differant frequencies. (o) ν_0 = 8MHz; (•) ν_0= 16MHz [1]. Solid line represents the theoretical curve.

$(CH_3)_4NMnCN_3$ (TMNC)[1], a best known Heisenberg antiferromagnetic chain with $T_N \sim 0.8$ K. The minimum in T_1^{-1} in the temperature range 300 - 1.5 K was reproduced theoretically on the basis of eq. 1 by assuming isotropic spin fluctuation and

$$S(\mathbf{q},\omega) = kT\chi(\mathbf{q},0)J_{\mathbf{q}}(\omega) = kT\chi(\mathbf{q},0)\frac{2\Gamma_{\mathbf{q}}}{\Gamma_{\mathbf{q}}^2+\omega^2}. \qquad (2)$$

The minimum in T_1^{-1} is understood by the following argument. At high temperature, the relaxation is dominated by the $\mathbf{q} = 0$ diffusive mode for

which $\Gamma_0 \sim 0$ and with lowering the temperature, the short range magnetic order develops and the $\mathbf{q} = 0$ fluctuations become less important as $\mathbf{q} = \mathbf{q}_c$ antiferromagnetic fluctuations are enhanced. Since this fluctuations, are less effective because of smaller geometrical factor C^i_α in eq. 1. The divergent behaviour below 15 K is due to critical enhancement and slowing down of the antiferromagnetic fluctuations.

4. Spin glasses

Spin glasses are the magnetic systems in which the interaction between the magnetic moments are in conflict with each other due to some frozen in structural disorder. Thus no conventional long range magnetic order can be established. Nevertheless, these systems exhibit a freezing transition to a state with a new kind of order in which the spins are aligned in random directions. The nature of these new kind of order, and its appropriate theoretical description, is still heavily debated. The classical spin glass materials are noble metals (Au, Ag, Cu, Pt) diluted with Fe or Mn. Here RKKY type exchange interaction is responsible for the spin glass transition. In insulators such transitions occur in systems where ferro and antiferromagnetic interactions co-exist, such as $Fe_{1-x}Mn_xTiO_3$. However, in case of Sr-Ga-Cu-O with only antiferromagnetic interaction the frustration appears due to typical symmetry of the magnetic lattice Fig.4 shows the beheaviour of low field χ_{ac}, and χ_{dc} in two spin glass systems[6,7]. The characteristic phenomena observed in spin-glasses are: 1. A cusp appears in χ_{ac} at T_f. χ_{ac} becomes, frequency dependent below T_f , indicating a considerable enhancement of the relaxation time of the magnetic ions. 2. Strong irreversibility in χ_{dc} for FC and ZFC experiments, below T_f reveals the significant influence of small magnetic field in aligning the atomic moments which are disordered below T_f. 3. Below T_f though there is no long range order, there is a remanent magnetisation when H=0 which decays to zero over a macroscopic time scale. Fig.5 shows the ^{57}Fe Mössbauer spectra [8] in Au-3 atomic % Fe system

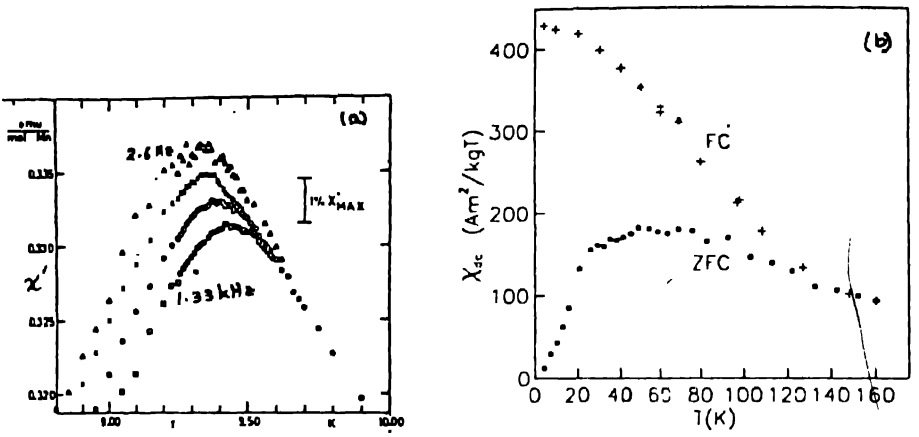

Fig.4 (a) Real part χ' of the complex susceptibility $\chi(\omega)$as a function of temperature for CuMn with 0.94 at % Mn[6]. (b) Temperature dependence of χ_{ZFC} and χ_{FC} for $Co_{50}Al_{47.5}Fe_{2.5}$ measured in the field of 1 Oe[7].

(in the temperature range 1.9-30 K and room temperature), which exhibit SG transition at 16.4 K. The results show there is a well defined change in the resonance line shape from about 19.5K which is well above T_f. In the region below 19.5K, the spectra were well described in terms of a static inhomogeneously broadened internal magnetic field distribution, which indicates that below T_f the local ordered magnetic field at different Fe sites are unequal. This result indicates the absence of a long range magnetic order below T_f. Above 19.5K, the spectra are compatible with relaxation broadening as discussed in sec. 2.

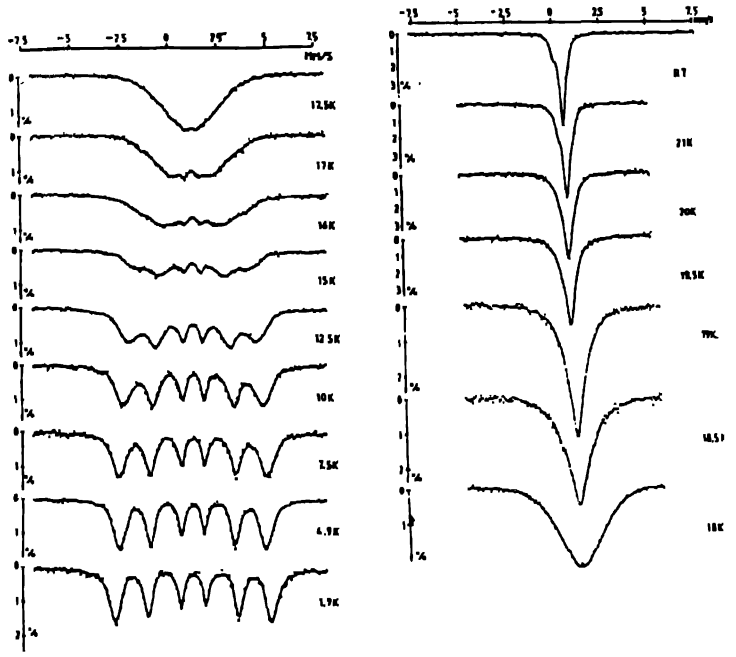

Fig.5 ^{57}Fe Mössbauer spectra in Au-3 atomic % Fe system in the temperature range 1.9 - 30K and at room temperature. Continuous line corresponds to the theoritical fit, using a Gaussian distribution of the hyperfine field [8].

5. **Heavy fermion (HF) systems.** The discovery of the formation of strongly correlated electron band at the Fermi level at low temperature in some Ce, Yb, and U intermetallic compounds [9] opened up a new area of research. In these systems the energy of the fundamental Kondo interaction, k_BT^*, competes with the indirect RKKY interaction, k_BT_{RKKY}. Whereas, the first interaction tends to form a non-magnetic singlet state well below T^*, the second one tends to arrest the Kondo reduction of the local f-derived magnetic moments. Since in HF compounds $k_BT^* \sim k_BT_{RKKY}$, a variety of ground state properties are observed. For $T_{RKKY}>T^*$, magnetic order develops below $T_m < T_{RKKY}$. For $T^*<T_{RKKY}$, a Pauli paramagnetic state is approached. In both the

cases the transition from normal to HF state occurs with a large enhancement in the electronic specific heat cofficient γ compared to a normal metal. Fig. 6 shows ^{63}Cu T_1^{-1} data of the systems $CeCu_6$, $CeCu_2Si_2$ and of ^{13}Be NMR in UBe_{13}[10]. The compound $CeCu_6$ when transforms from normal to HF state, the electronic behaviour changes from normal paramagnet to a Pauli paramagnet as observed from T_1^{-1} data. Above 6 K (T_K), T_1^{-1} is almost temperature independent corresponding to Curie-Weiss behaviour of the susceptibility and below 6 K, T_1^{-1} follows the Korringa relation like a Pauli paramagnet. On the other hand $CeCu_2Si_2$ and UBe_{13} which undergo a superconducting transition below 1 K in the HF state, shows a continuous decrease of T_1^{-1} with T^3 in the superconducting state in contrast to a BCS superconductor, which shows an enhancement just below T_c. This result provides an evidence for the unconventional nature of the superconductivity in HF systems.

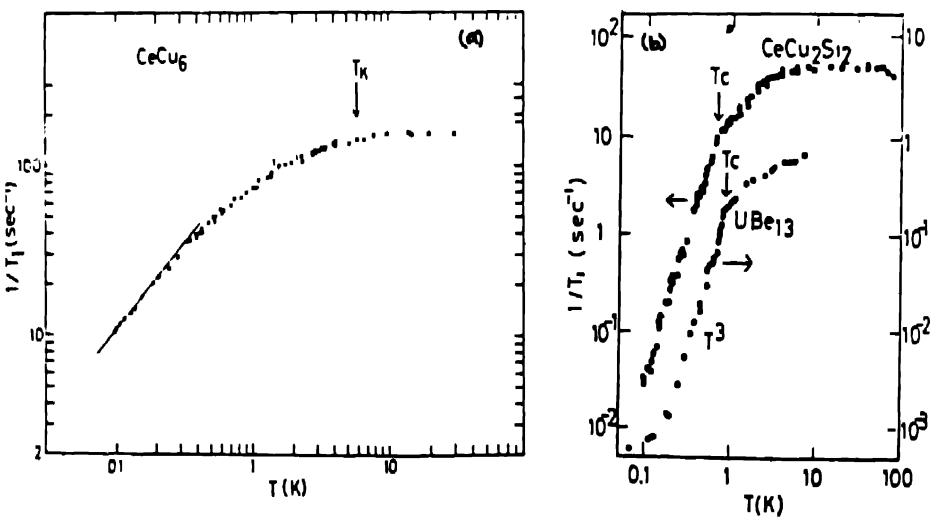

Fig. 6 a) T_1^{-1} of ^{63}Cu in $CeCu_6$, b) T_1^{-1} of ^{63}Cu in $CeCu_2Si_2$ and ^{13}Be in UBe_{13} [10].

References

[1] F. Borsa and A. Rigamonti in Magnetic resonance of phase transitions (ed. F. J. Owens, C. P. Poole, Jr. and H. A. Farach, Academic press. 1979).

[2] M. E. Fisher, Rep. Prog. Phys. **30**, 615, 1979.

[3] L. J. De Jongh and A. R. Meidema, Adv. Phys. **23**, 1, (1974).

[4] K. Ghoshray, A. Ghoshray and N. Chatterjee, Phys. Rev. **B 42**, 7803, (1990) and references therein.

[5] P. Heller, and G. B. Bendek, Phys. Rev. Lett. **8**, 428, (1962).

[6] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801, (1986).

[7] E. Lähderanta, K. Eftimova, R. Laiho, H. Al Kanani, J. G. Booth, J. Mag. Mag. Mat. **130**, 23, (1994).

[8] C. Mayer, F. Harzmann-Boutron and Y. Gross, J. Mag. Mag. Mat. **46**, 254, (1985).

[9] G. R. Stewart, Rev. Mod. Phys. **56**, 755, (1984).

[10] K. Asayama, Y. Kitaoka and Y. Kohari, J. Mag. Mag. Mat. **76 & 77**, 449, (1988).